

Composition pour modifier les fibres de kératine

Patent number: FR1503640

Publication date: 1967-12-01

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Classification:

- international:

- european: A61K7/09B, A61K7/13B, A61K7/155, D06M11/52, D06M11/54, D01F4/00

Application number: FR19660076969 19660920

Priority number(s): US19650488759 19650920

Also published as:



GB1164103 (A)

DE1619064 (A)

BE687130 (A)

Abstract not available for FR1503640

Abstract of correspondent: **GB1164103**

1,164,103. Depilating hides. GILLETTE CO. Sept.20, 1966 [Sept.20, 1965], No.41845/66. Heading C6C. [Also in Division D1] Animal hair is removed from hides by applying thereto an aqueous composition containing (1) a reducing agent selected from water-soluble sulphites, bisulphites and hydrosulphites and (2) an oxidizing agent selected from water-soluble tri- thionates, tetrathionates, pentathionates and hexathionates, the molar ratio of oxidizing agent to reducing agent being from 0A05:1 to 1:1 except when the oxidizing agent is a trithionate when the ratio is from 0A05:1 to 2:1 and then removing the hair by rubbing or scraping. The treating com- position may be prepared by adding a dry finely divided particulate solid composition comprising the reducing agent and oxidizing agent to water, the aqueous composition preferably containing 0A1-4 moles per litre of the reducing agent. The cations of the treating agents may be ammonium, alkali metal or mono, di- or tri-lower alkanolamine salts. The treating composition may have a pH of 4A5-11 preferably adjusted by the addition of ammonium hydroxide and may contain a swelling agent, e.g. urea, isopropanol, lithium bromide or phenol, preferably in an amount of 1-8 moles pe mole of reducing agent. The treatment may be effected at from room temperature to the boiling point of the solution.

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Composition pour modifier les fibres de kératine

Description of correspondent: GB1164103

COMPLETE SPECIFICATION

Composition for Modifying Keratin Fibres

We, THE GILLETTE COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of

Gillette Park, Boston, Massachusetts, United

States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :

This invention relates to a composition and method for the chemical modification of keratin-containing fibers. Such modification may be used in the depilation of animal hair from hides or in imparting to wool resistance to felting and shrinkage during laundering or in increasing the ease with which such fibers, including human hair, may be dyed.

The keratin-containing fibers to which the present invention relates include both human hair and animal hair, such as wool, including wool textile fabric.

The invention provides a composition and method for modifying keratin-containing fibers to permit them to be softened or dissolved under mild conditions, i.e. at moderate temperatures without the necessity for using strong alkali.

It has now been found that dry (i.e. substantially free from water) finely divided particulate solid compositions comprising mixtures of water-soluble reducing agents which are sulfites, bisulfites, or hydrosulfites with water-soluble oxidizing agents which are trithionates, tetrathionates, pentathionates, or hexathionates are effective, when dissolved in an aqueous medium, to react with keratin-containing fibers at room temperature or elevated temperature to convert the disulfide linkages of the keratin into the S-sulfo form with concomitant swelling and softening of the fiber.

Among the materials which may be used are the ammonium and alkali metal and mono-, di-, or tri-lower alkanolamine salts of the foregoing anions. The mixture may contain compounds having different cations as well as the same cations.

By means of the present invention the extent to which the fibers may be reacted is much greater than can be achieved when the reducing agent alone is used to react with the fibers. The compositions in either dry form or in the form of aqueous dispersion or solution are nontoxic when applied to the skin. The compositions in dry form are very stable and may be stored over long periods of time. After the addition of water to form a solution or slurry, however, the composition is relatively unstable and should not be stored for an extended period of time before use.

While the mechanism of the reactions may not be fully understood and we do not wish to be bound by the following theory, it is believed that tetrathionate, pentathionate and hexathionate react with the reducing agent to form a trithionate; in the case of tetrathionate, one mole of sulfite reducing agent reacts with each mole of tetrathionate to form the trithionate; in the case of pentathionate, two moles of sulfite react to form trithionate; and in the case of hexathionate, three moles of sulfite react to form trithionate. The general equation for such reaction is:

$$\text{EMI } 1.1$$

where n is the integer 4, 5 or 6. It is also believed that no rapid reaction occurs between the trithionate and the reducing agent but that the reducing agent reacts with the disulfide - linkages in the keratin to form an S-sulfo group and a thiol group from each such linkage, and that the trithionate oxidizes each thiol group thus produced back to the disulfide form.

The relative proportions of reducing agent and of oxidizing agent may vary over a considerable range; when only sulfite and trithionate are present, for example, any mole excess of trithionate over the sulfite does not improve the effectiveness of the composition in modifying keratin fibers, but it does increase the rate of reaction, especially when the concentration of sulfite is relatively low; an excess of sulfite over trithionate, however, is available for reacting with the keratin as pointed out above. When sulfite and tetrathionate or higher polythionates are in the mixture some of the sulfite reacts with the polythionate leaving only the balance to react with the keratin; under these circumstances an excess - of the reducing agent is preferred. According to the invention from 0.05 to 1 mole of oxidizing agent is present for each mole of reducing agent, except that when the oxidizing agent is a trithionate, from 0.05 to 2 moles of oxidizing agent is present for each mole of reducing agent.

The concentration of reducing agent and oxidizing agent in the aqueous solution or slurry may vary widely. - In general, the composition may contain from 0.1 to 4 moles per liter of reducing agent, together with from 0.05 to 1 mole of oxidizing agent (or in the case of a trithionate 0.05 to 2 moles) for each mole of reducing agent. The aqueous composition may have a pH from 4.5 to 11, but the reaction proceeds most rapidly at pH 6 to 7. When the invention is employed to treat wool to shrink-proof it or to render it more susceptible to dyeing, it is preferred to employ a short treatment of the keratin fiber with the aqueous composition at a pH value above 8 so as to obtain maximum conversion of the sulfide linkages in the surface portion of the keratin fibers with minimum conversion of the disulfide linkages in the interior of the fiber.

On the other hand, when uniform modification of the entire keratin fiber is desired the best results are obtained using longer treatment of the fibers with the composition at a pH value of 8 or below. While any conventional alkaline material may be used for adjusting the pH if desired, ammonium hydroxide is usually preferred. If desired, any of the conventional buffer salts may be used to maintain the pH within the desired range.

There may also be incorporated in the composition protein-swelling agents such as urea, isopropanol, lithium bromide and phenol. These swelling agents increase the rate of formation of S-sulfo groups as well as enhance the swelling of the keratin fibers.

When - used, such swelling agents generally may be present in amounts up to 8 moles per mole of reducing agent, preferably from 1 to 8 moles per mole of reducing agent, the exact amount present depending upon the identity of the particular swelling agent employed and upon the effect desired. If excessive amounts are present they may be insoluble, or may cause salting out of other ingredients. When the composition is to be used for dehairing hides, the presence of such swelling agents is particularly desirable.

When it is desired to confine the effect of the composition to the surface of the keratin fiber and to minimize swelling, as for example in the process of shrink-proofing wool, there may be included in the composition a swelling agent such as a water-soluble salt which is chemically inert to the oxidizing agent and reducing agent and to hair keratin such as sodium chloride, potassium chloride, sodium sulfate - and magnesium sulfate, - generally - in amounts up to 4 moles per mole of reducing agent, preferably from 0.5 to 4 moles per mole of reducing agent, the precise amount present depending upon the identity of the salt and the effect desired, as in the case of swelling agents.

- Upon - using the composition it is first mixed into an aqueous medium and then applied to the keratin fibers, either at room temperature or at elevated temperatures which may be as high as the boiling point of the solution when it is used for dehairing hides or for shrink-proofing wool. However, in general, it is preferred to use temperatures from room temperature up to 400°C.

The method of the invention produces a high proportion of S-sulfo groups (R-S-SO₃- groups) in the fibers in a single step, without the use of a metal catalyst. The stable, dry keratin fiber thus produced is substantially free from metal, and has its chemical composition modified by the rupture of from 10% to 70% of its disulfide linkages and formation of S-sulfo groups. This enhances its dyne receptivity and improves its setholding characteristics.

In making use of the compositions of the present invention for dehairing hides, the aqueous composition is simply left in contact with the keratin fibers for a sufficient period of time to swell and soften the fibers so that they may readily be removed from the hide by gentle rubbing or scraping.

The following specific examples are intended to illustrate the invention more clearly without limiting the scope thereof.

Example I

There were prepared a series of aqueous solutions each containing 1 molar ammonium bisulfite and containing sodium tetrathionate in varying concentrations as set forth in the table below. Each solution was adjusted to pH 7 by ammonium hydroxide. There was immersed for 30 minutes in a 50 ml. portion of each solution at 35°C. a 1 gram sample of brown European human hair. Each hair sample was then removed from the solution and rinsed in running water for 5 minutes, during which time most remaining pairs of thiol groups and S-sulfo groups recombined to form disulfide linkages. The extent to which S-sulfo groups remained in the keratin fiber without being reconverted to the disulfide linkage was then determined by first alkylating any remaining thiol groups by immersing the hair for 15 minutes in a molar aqueous solution of acrylonitrile at pH 9.2, then hydrolyzing the hair by immersing for 2 hours at 105°C. in 25 ml. of 30 percent sulfuric acid to convert the remaining S-sulfo groups into thiol groups, the concentration of which was then determined by titration with 0.1% (3-hydroxymercuri-2-methoxypropyl) carbamyl-phenoxycetic acid, using

sodium nitroprusside as an indicator. The titer is reported in the following table as milliequivalents of irreversible (i.e. irreversible by dilution of the solution) S-sulfo groups per gram of hair.

Concentration of Sodium Irreversible S
Tetrathionate, Molarity sulfo Groups

0.0 0.08
0.2 0.65
0.4 0.68
0.6 0.63
0.8 0.42
1.0 0.22

The results set forth in the table clearly show that the presence of even a small proportion of sodium tetrathionate in the solution leads to a remarkable increase in the number of irreversible S-sulfo groups present in the keratin fiber and that the effectiveness of the mixture decreases when the amount of sodium tetrathionate approaches the amount of ammonium bisulfite present. Even when the molar concentration of reducing agent and oxidizing agent in the solution is the same, however, the effectiveness of the solution of the mixture is very much greater than that of a solution of The reducing agent alone because the reaction between the sodium tetrathionate and the ammonium bisulfite is an equilibrium reaction, leaving some ammonium bisulfite available to react with the hair keratin.

Example 2

The same procedure was followed as in

Example 1 above except that sodium trithionate was substituted for sodium tetrathionate. The result obtained are set forth in the following table.

Concentration of Sodium Irreversible S
Trithionate, Molarity sulfo Groups

0.0 0.08
0.1 0.56
0.2 0.77
0.3 0.81
0.4 0.84
0.5 0.86
0.75 0.89
1.0 0.88

The results clearly show that the presence of a small amount of sodium trithionate in the aqueous solution produces a very large increase in the proportion of irreversible S-sulfo groups formed in the keratin fiber and also show that the effectiveness of the mixture does not decrease when the amount of sodium trithionate approaches the amount of reducing agent. - See Example 1;

- The RTI procedure of Example 1 was followed but sodium pentathionate was substituted for sodium tetrathionate. The results were as set forth in the following table.

Concentration of Sodium Irreversible S
Pentathionate, Molarity sulfo Groups

0.0 0.08
0.2 0.50
0.5 0.65

These results also demonstrate the superior effectiveness of the aqueous solution of the mixture as compared with an aqueous solution of the reducing agent alone.

Example 4

A solution was prepared - by dissolving in water a mixture of sodium hydrosulfite and sodium trithionate, the concentration of the hydrosulfite being 0.6 molar and that of the trithionate being 0.2 molar, so that the mole ratio of oxidizing agent to reducing agent was approximately 0.33 : 1. The pH of the solution was adjusted to 7 by means of ammonium hydroxide; There was immersed in a 50 ml. portion of this solution maintained at 35 C. 1 gram of brown European human hair for 6 hours. The hair was then removed rinsed in water and the concentration of irreversible S-sulfo groups was determined as described in Example 1 and found to be 0.69 milliequivalents per gram.

Example 5

A mixture of 13.5 g. sodium tetrathionate (50 millimoles), 6.1 g. of sodium sulfite (50 millimoles), and 5.4 g. of sodium bisulfite (50 millimoles) was triturated and - stored in a loosely covered container. This particulate solid mixture was then dissolved in water to make 100 ml. of solution having a pH of 7. One gram of brown European human hair was immersed in the solution maintained at 35 C. for 30 minutes. After removal from the solution and rinsing the irreversible S-sulfo group content of the treated hair was found to be 0.33 milliequivalents per gram.

A 0.5 0.2 None None 8.8

B 1.0 0.2 None None 0.6

C 1.0 0.2 None 3 0.6

D 1.0 None 0.2 None 0.7

Untreated 29.2

All of the specimens had a satisfactory hand and appearance after the treatment, sample C being the best.

Example 10

There was prepared an aqueous solution containing 1 molar ammonium bisulfite and 0.2 molar sodium trithionate, and it was adjusted to pH 7 by adding ammonium hydroxide. Several different swatches of undyed wool flannel measuring 6 inches by 6 inches were immersed in individual 100 ml.

portions of the solution, some for 10 minutes at 35 C., others for 30 minutes at 25 C.

The swatches were then removed, rinsed thoroughly with water, and then with an aqueous solution containing 0.05 molar borax to cause any residual thiol groups in the keratin fiber to recombine with the S-sulfo groups.

Portions of the treated swatches along with an untreated swatch as control were then dyed by immersion in solutions of basic dyes and acid dyes. In all cases the treated swatch was markedly more deeply dyed than was the untreated control.

Example 11

There were prepared 50 ml. portions of aqueous solution containing 0.6 molar ammonium bisulfite, 0.3 molar sodium tetrathionate, and 0.3 molar urea, adjusted with aqueous ammonia to pH 6. A one gram sample of brown European hair was immersed in each portion while maintained at 35 C. Pairs of samples were withdrawn from the solution after predetermined times.

One of these was immediately rinsed with hydrochloric acid (1 normal) to stop the rupture reaction from proceeding further, and then hydrolyzed and analysed for thiol content; the value so obtained is considered to represent the total rupture level of sulfide linkages existing in the keratin at the time of immersion in acid, reflecting both the thiol and S-sulfo groups present; the other sample was rinsed with water, and treated with acrylonitrile as described in Example 1, prior to hydrolysis and analysis to determine the quantity of irreversible S-sulfo groups present. The results are recorded in the following table.

Irreversible

Treatment Total Rupture S-sulfo Groups
Time Milliequivalents Milliequivalents
Minutes per gram per gram

5 0.29 0.09

10 0.49 0.18

15 5.8 0.28

22q 0.68 0.37

30 0.74 0.54

It is evident that under the conditions used here, the total rupture proceeds more rapidly in the initial stages than the formation of irreversible S-sulfo groups. However, the rate of rupture slows down after the first 10-15 minutes, whereas irreversible S-sulfo groups continue to be generated at a constant rate; consequently, after 30 minutes, almost three quarters of the rupture is in the form of irreversible S-sulfo groups.

Example 12

One-gram samples of brown European hair were each immersed for 10 minutes at 35 C. in 50 ml. portions of solutions of the following composition: 0.6 molar ammonium bisulfite, 0.2 molar sodium tetrathionate, and 3 molar urea, the pH being adjusted to various values by means of aqueous ammonia. The total rupture level and the irreversible S-sulfo group content were determined by the methods described in Examples 1 and 4. The following results were obtained.

Irreversible

Total Rupture S-sulfo Groups
Milliequivalents Milliequivalents
pH per gram per gram

7.0 0.44 0.24

8.0 0.36 0.29

9.0 0.30 0.26

9.7 0.25 0.25

These data demonstrate that the amount of irreversible S-sulfo groups generated as a proportion of the total extent of rupture in a short treatment may be varied by appropriate selection of pH of the reaction.

the extent of rupture, in a short treatment, may be varied by appropriate selection of pH of the reaction medium. As the pH is raised, the rate of total rupture decreases, but the proportion of irreversible S-sulfo groups increases.

Microscopic examination of the course of the reaction between keratin fibers and sulfite solutions has shown that the slower rate of reaction at high pH is associated with a slow rate of penetration of the reagent into the fiber.

Example 13

An aqueous solution was prepared containing 1 molar ammonium bisulfite, 4 molar urea, and 0.4 molar potassium tetrathionate, and adjusted to pH 8 by means of ammonia.

A tress of European human hair, weighing 4 g., was immersed in 10 ml. of this solution, at 32 C. After one hour, the tress was thoroughly rinsed with water and shampooed. Two additional similar tresses were treated with media of the same composition but diluted with one or two volumes of water per volume of solution respectively.

Single fibers were removed from the tresses and cut in half to provide duplicate fiber specimens. The radius of curvature of each piece was determined; it was then placed, wet, in a circular form 5/8" diameter. Knowing the original radius of curvature of each specimen, and the diameter of the form, the level of strain imposed on each sample could be calculated.

The forms containing the fibers were then maintained at 100% relative humidity for one hour and subsequently at 32% relative humidity for 18 hours to give the fibers a set. The fibers were then taken out of the forms and placed in an atmosphere of 65% relative humidity; the subsequent increase in radius of curvature of the fiber arc was followed over a period of two hours. The "strain ratio", reported in the table below, represents the strain retained by the fiber after two hours relaxation divided by the imposed strain. The higher the strain ratio, the greater the extent to which the hair fiber retained the strain imposed upon it in the 5/8" circular form.

| Concentration of Solution | Irreversible S-sulfo Groups | Strain Ratio |
|---------------------------|-----------------------------|--------------|
| Full Strength | 0.84 | 0.98 |
| 0.5 | 0.44 | 0.52 |
| 0.33 | 0.24 | 0.40 |

Untreated control fiber - - 0.34

It is evident that, as the irreversible Ssulfo group content increases, the strain ratio increases also; in other words, the setholding ability of the hair is improved.

Example 14

There was prepared a slurry containing 13.5 g. of sodium tetrathionate (50 millimoles), 6.1 g. of sodium sulfite (50 millimoles), 5.4 g. of sodium bisulfite (50 millimoles), and 30.6 milliliters of isopropanol (400 millimoles). The slurry was found to be stable upon storage in a stoppered container. Shortly before use, sufficient water was added to make 100 milliliters of total composition, having a pH of 6.7.

Two grams of brown European hair were immersed in this solution, maintained at 35 C., for 30 minutes, to form S-sulfo groups.

The hair was then rinsed; the extent of its swelling in a buffer at pH 7 was determined, and found to be 167%.

Keratin fibers and textile fabrics treated in accordance with the present invention may be rinsed with water and dried without loss of the irreversible S-sulfo groups. The fibers and fabrics retain their increased dye receptivity, set-holding ability, and felting resistance indefinitely. When such fibers and fabrics are treated with an aqueous solution of sulfite alone, however, they lose their Ssulfo groups when in contact with wash water, reverting to the properties of untreated materials.

Such stable keratin fibers are those having from 10% to 70% of their disulfide linkages ruptured, at least half of the side chain end groups resulting from the rupture being irreversible S-sulfo groups, i.e. S-sulfo groups which do not recombine with thiol groups in the molecule when the fibers are rinsed with water. Such fibers are free from metal since no metal catalyst is used in the process of the present invention.

WHAT WE CLAIM IS:

1. A dry finely divided particulate solid composition for use in the chemical modification of keratin-containing fibers, comprising a mixture of (1) a reducing agent selected from water-soluble sulfites, bisulfites and hydrosulfites with (2) an oxidizing agent selected from water-soluble trithionates, tetrathionates, pentathionates and hexathionates, the molar ratio of oxidizing agent to reducing agent being

from 0.05:1 to 1:1 except when the oxidizing agent is a trithionate when said ratio is from 0.05:1 to 2:1.

2. A composition as claimed in claim 1 which also includes a protein-swelling agent, the molar ratio of swelling agent to reducing agent being from 1:1 to 8:1.

3. A composition as claimed in claim 1 or 2, which also includes a water-soluble salt which is chemically inert to said oxidizing agent and reducing agent and to hair keratin, the molar ratio of inert salt to reducing agent being from 0.5:1 to 4:1.

4. A composition as claimed in claim 1, substantially as hereinbefore described with reference to the foregoing Examples.

5. A method of modifying the properties of keratin-containing fibers which comprises contacting said fibers with an aqueous composition containing (1) a reducing agent selected from water-soluble sulfites, bisulfites and hydrosulfites and (2) an oxidizing agent selected from water-soluble trithionates, tetrathionates, pentathionates and hexathionates, the mole ratio of oxidizing agent to reducing agent being from 0.05:1 to 1:1 except when the oxidizing agent is a trithionate when said ratio is from 0.05:1 to 2:1 and the concentration of reducing agent being from 0.1 to 4 moles per liter of said composition.

6. A method as claimed in claim 5, substantially as hereinbefore described with reference to the foregoing Examples.

7. Keratin fiber free from metal having from 10% to 70% of its disulfide linkages ruptured, at least half th

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Claims of correspondent: **GB1164103**

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set. The fibers were then taken out of the forms and placed in an atmosphere of 65% relative humidity; the subsequent increase in radius of curvature of the fiber arc was followed over a period of two hours. The "strain ratio", reported in the table below, represents the strain retained by the fiber after two hours relaxation divided by the imposed strain. The higher the strain ratio, the greater the extent to which the hair fiber retained the strain imposed upon it in the 5/8" circular form.

Concentration Irreversible
of Sulfonation S-sulfo Groups Strain Ratio
Full Strength 0.84 0.98
0.5 0.44 0.52
0.33 0.24 0.40

Untreated control fiber -- 0.34

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Two grams of brown European hair were immersed in this solution, maintained at 35° C., for 30 minutes, to form S-sulfo groups.

The hair was then rinsed; the extent of its swelling in a buffer at pH 7 was determined, and found to be 167%.

Keratin fibers and textile fabrics treated in accordance with the present invention may be rinsed with water and dried without loss of the irreversible S-sulfo groups. The fibers and fabrics retain their increased dye receptivity, set-holding ability, and felting resistance indefinitely. When such fibers and fabrics are treated with an aqueous solution of sulfite alone, however, they lose their S-sulfo groups when in contact with wash water, reverting to the properties of untreated materials.

Such stable keratin fibers are those having from 10% to 70% of their disulfide linkages ruptured, at least half of the side chain end groups resulting from the rupture being irreversible S-sulfo groups, i.e. S-sulfo groups which do not recombine with thiol groups in the molecule when the fibers are rinsed with water. Such fibers are free from metal since no metal catalyst is used in the process of the present invention.

WHAT WE CLAIM IS:

1. A dry finely divided particulate solid composition for use in the chemical modification of keratin-containing fibers, comprising a mixture of (1) a reducing agent selected from water-soluble sulfites, bisulfites and hydrosulfites with (2) an oxidizing agent selected from water-soluble trithionates, tetrathionates, pentathionates and hexathionates, the molar ratio of oxidizing agent to reducing agent being from 0.05:1 to 1:1 except when the oxidizing agent is a trithionate when said ratio is from 0.05:1 to 2:1.
2. A composition as claimed in claim 1 which also includes a protein-swelling agent, the molar ratio of swelling agent to reducing agent being from 1:1 to 8:1.
3. A composition as claimed in claim 1 or 2, which also includes a water-soluble salt which is chemically inert to said oxidizing agent and reducing agent and to hair keratin, the molar ratio of inert salt to reducing agent being from 0.5:1 to 4:1.
4. A composition as claimed in claim 1, substantially as hereinbefore described with reference to the foregoing Examples.
5. A method of modifying the properties of keratin-containing fibers which comprises contacting said fibers with an aqueous composition containing (1) a reducing agent selected from water-soluble sulfites, bisulfites and hydrosulfites and (2) an oxidizing agent selected from water-soluble trithionates, tetrathionates.